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The Application of Amalgam Metallurgy to Copper

Barry J. Hansen

THE APPLICATION OF AMALGAM METALLURGY TO COPPER

A Thesis
Submitted to
The Department of Metallurgy
Montana School of Mines
Butte, Montana

In Partial Fulfillment
of the Requirements for the Degree
Bachelor of Science in Metallurgical Engineering

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TABLE OF CONTENTS

TABLES AND FIGURES

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I. The Problem

The object of this investigation is the application of "Amalgam Metallurgy" to the extraction of copper from its ores. "Amalgam Metallurgy" as defined by Hohn is the use of liquid mercury in the extraction of metals.[1] The ore under study was from the Kelly Mine in Butte, Montana and contains about 1.0% copper of which about 0.1% is acid soluble.

The present method for treating this ore involves several steps. The crushed ore is first leached with dilute sulfuric acid and the acid soluble copper is separated from the sulfide minerals, which are sent to flotation for concentration of the remaining copper minerals. The copper in solution is then precipitated with sponge iron and the resulting cemented copper is concentrated by flotation. The concentrated copper cement is then sent to the smelter where the copper is extracted in the usual manner involving matte smelting, converting, and refining. As can be seen this method involves many expensive operations and at low metal prices proves to be uneconomical.

The use of electrolysis involving mercury electrodes could cut the number of steps to three. The ore would first be leached and the solution clarified and sent to

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[1] H. Hohn, "Mercury in Chemical Metallurgy", Research, 3;20, January, 1950.

to an electrowinning cell where the copper would be plated into a mercury cathode utilizing an inert anode. The amalgam would be transferred to another cell where it would become the anode and a pure copper starting sheet the cathode. The result of these three steps would be electrolytically pure copper.

II. INTRODUCTION

While there exists a great deal of literature concerning the metallurgy of copper, and the use of the mercury electrode in analytical chemistry has had wide acceptance, there has been little written dealing with the amalgam metallurgy of copper. The best references on the role of mercury in metallurgy are by Dr. H. Hohn.

Hohn divides metals into three classifications, according to their affinity for mercury. (1) The Iron types are those metals which have a low affinity for mercury and amalgamate only at the surface. These metals form dispersoids in mercury. (2) The Zinc types are those metals having a medium affinity for mercury and readily form true amalgams. (3) The Sodium types include the more reactive metals which have a high affinity for mercury and combine violently to form very stable amalgams. The Zinc types are those metals which are grouped near Mercury in the periodic table. They include Zn, Cd, In, Ga, Pb, Au, Ag,

Cu and some others. It is the application of amalgam metallurgy to this group of metals that shows the greatest promise.[2]

Hohn also lists three types of electrolysis involving amalgams: (1) semi-electrolysis, the passing of one metal from the amalgam to the aqueous phase while other metals remain inert in the amalgam; (2) blocking-electrolysis employing the amalgam as the anode in contact with a pure solution of the metal desired to be extracted from the amalgam (in this case the mercury acts as a barrier preventing all but the desired metal from depositing); and (3)indirect-electrolysis involving two steps, first the mercury is used as a cathode to collect the metals; then the mercury is placed in contact with an aqueous solution to allow a phase exchange to take place.[3]

The behavior of amalgams in chemical reactions is governed by the following rules: (1) the potential of an amalgam is determined by its least noble component; (2) each amalgam strives to attain a more positive potential. Those reactions which produce a more positive potential proceed spontaneously. (3) An amalgam is unable to take part in a reaction

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[2] H. Hohn, "Applications of Amalgam Metallurgy", Reseach, 3:407, September, 1950.

[3] Ibid.

which does not change its potential. The potential of an amalgam in contact with a solution containing ions of other the other metal in the amalgam is expressed mathmatically below.

$$E = E_o - \frac{RT}{nF} \ln \frac{C_{H2O}}{C_{Hg}}$$

or

$$E = K - \frac{0.058}{n}(\log C_{H2O} - \log C_{Hg})$$ [4]

Theoretically it is possible to apply amalgam methods to the extraction of metals from low grade solutions with a high degree of selectivity. This, however is not the only application of mercury to the field of metallurgy.

Pure metal powders, suitable for powder metallurgical applications can be prepared by dry mercury evaporation. Alloys may be prepared electrolytically in the same manner and with the same ease as can metals. Metals in amalgams can react with soluble components of a solution and precipitate them. Example: Lead in an amalgam will react with copper in solution and precipitate it.[5]

These few examples indicate that the field of amalgam metallurgy offers much promise and is deserving of greater investigation.

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[4] Ibid.

[5] Ibid.

III. MERCURY IN ELECTROLYSIS

Mercury cathodes have been used for quite some time in the field of analytical chemistry in determining the reduction potential of an ion or the separation of an ion from a solution by carefully controlling the potential. This type of analysis, in which one electrode in the cell consists of mercury falling dropwise from a fine-bore capillary tube into a solution containing oxidizable or reducible substances, is called polarography. A graph of current versus voltage, called a polarograph, gives both a qualitative and quantitative analysis of the solution. The half-wave potential of an element is the potential at the point where a polarographic wave has reached its half-amplitude. This potential is an exact measure of the potential necessary to reduce a substance at a mercury cathode. It is characteristic of the element and does not vary with ion concentration.[6]

Another quality of the mercury cathode is the large negative hydrogen overpotential which allows the deposition of metals much more active than hydrogen at a mercury cathode. Hydrogen overpotential is the potential over the theoretical which is necessary to form gaseous hydrogen at a cathode from an aqueous solution of hydrogen ions. Overpotential is dependent upon many factors, such as current density, temperature, composition of the electrolyte, concentration

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6. Farrington Daniels, Robert A. Alberty, Physical Chemistry, (New York; John Wiley & Sons Inc.,1955), p405.

of hydrogen ions in solution, cathodic material, and other variables.

The following table demonstrates the hydrogen overpotential of mercury as compared to other cathode materials. It will be noted that a large potential in excess of the theoretical must be applied to a mercury cathode to discharge hydrogen. It is this large overpotential that allows metals more active than hydrogen to be deposited from an aqueous solution.

Table 1

Overpotentials in N-Sufuric Acid Solution[7]

Platinized platinum	-0.005 volt
Gold	-0.02 "
Polished platinum	-0.09 "
Silver	-0.15 "
Nickel	-0.21 "
Copper	-0.23 "
Cadium	-0.48 "
Tin	-0.53 "
Lead	-0.64 "
Zinc	-0.70 "
Mercury	-0.78 "

The quantity of metal liberated during electrolysis is determined by Faraday's laws of electrolysis. These laws may be expressed as:

1. The mass of a substance liberated in an electrolytic cell is proportional to the quantity of electricity passing through the cell.
2. When the same quantity of electricity is passed

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[7] S. Glasstone, The Electrochemistry of Solutions, (London: Methuen and Company, 1930) p374.

through different cells, the masses liberated are proportional to their chemical equivalents.

IV. EQUIPMENT

Leaching was carried out in a 4000 ml beaker. Agitation of the pulp was provided by a Brookfield Counter Rotating Mixer Model L, powered by a Superior Electric Company Powerstat. The lixivant used was 3N sulfuric acid. The solution was separated and clarified by using a vacuum flask filter utilizing Watman No. 2 filter paper.

Direct current for electrolysis was provided by a Welch Company rectifier. The A.C. current to the rectifier was controlled by a Superior Electric Company Powerstat. A Weston dc ammeter, Model 280, was employed to approximate the current flowing through the circuit. A Weston dc voltmeter, Model 280, range 0-30v, was utilized to check the voltage across the cell. A copper coulometer connected in series with the cell was used to determine the exact amount of current passing through the cell. A 115 volt magnetic stirrer was used to agitate the mercury to prevent polarization of the cathode and to expose a continous fresh surface for amalgamation. The cell used was a 400 ml beaker. A 2in by 4½ in commercially pure lead strip was used as an inert anode in stripping the leach solution. A copper sheet of the same dimensions served as the cathode in the refining step.

Qualitative analysis of the cell products was carried out with a North American Phillips Company type No. 12045.

Diffraction and Spectrograph unit. Quantitative analysis of the solutions was carried out by Mr. C. J. Bartzin.

V. PROCEDURE

The first step in the investigation was the preparation of the copper bearing solution for electrolysis. Two hundred grams of Kelly ore were made up into a 25% solids pulp with 3N sulfuric acid. Sulfuric acid was chosen for the solvent because of its solvent action on the oxidized copper minerals.[8] The leach was allowed to proceed for 30 minutes after which the solution was filtered and clarified.

Three hundred milliliters of the clarified solution were placed in the cell in contact with a pool of mercury which covered the bottom of the cell. The solution was then electrolyzed for 30 min.,at which time the solution had lost its blue color signifying the complete removal of the copper. The purpose of this test was to prepare an amalgam for furthur testing. No attempt was made to secure the highest current efficiency and it was correspondly low, 65.8%. Rough tests on the electrolyzed solution showed the complete removal of copper and the removal of most of the iron. Tests were conducted later to determine the most

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[8] John D. Sullivan, "Chemical and Physical Features of Copper Leaching", Transactions of the American Institute Mining and Metallurgical Engineers, Copper Metallurgy, Vol. 106, New York, (1933), p 515.

efficient time for electrolysis. Previous work by Alexander has indicated the optimum current density for electrolysis of a copper sulfate solution to be 20 amps per square foot.[9]

An attempt was next made to remove the copper from the amalgam. This necessitated the reversal of the cell's polarity. In this first attempt, the tailings from the previous step were used as the electrolyte. This test proved to be a failure. The amalgam polarized and a substance believed to be mercurious sulfate formed while mercury plated out on the copper cathode. Another test was made utilizing the head solution for the electrolyte; results similar to the first test were obtained and the test was considered a failure. In these tests the voltage was varied in order to find the correct potential for electrolysis.

At the time, it was thought that the behavior noticed above was due to some impurity either in the mercury or in the solutions. It was then decided to make up pure solutions and to distill the mercury. A pure solution of approximately 10 grams per liter of copper sulfate was made up to serve as an electrolyte and as a source of copper for the amalgams. Due to breakage of the mercury still, only a small amount of mercury was distilled and that only once. However, it was thoroughly washed with dilute nitric acid

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[9] John A. Alexander, "The Effect of Iron on the Electrowinning of Copper with an Amalgam Electrode", B.S. Thesis, Montana School of Mines, Butte, Montana, (1952), p 11.

and was assumed to be of sufficient purity for the purposes of this investigation.

The usual procedure was followed in the next test with the pure materials. The solution was electrolyzed to prepare the pure amalgam. The current efficiency of this step was very good, 98.8%. The amalgam was made the anode and the process of varying the voltage from 0 to 11 volts was repeated. Again the same results were noted. This test failed to produce copper but it indicated that the previous failures were not due to impurities but to a more fundamental reason.

The next test was made to determine the joint effect of concentration of copper in the amalgam and a change of electrolyte. The following reaction is believed to have occured in the previous tests.

$$2Hg \rightleftharpoons Hg_2^{++} + 2e^-$$

The potential at which this reaction takes place depends upon whether or not the solution contains substances which form insoluble salts or stable complexes with mercury and it ranges from -0.6 volts versus a Standard Calomel Electrode to -0.4 volts vs. (Standard Calomel Electrode).[10]

For the above reason it was decided to try using a copper chloride solution having a strength of 10 grams per liter $CuCl_2$ for the electrolyte. As was stated before, the

[10] I.M. Kolthoff and James J. Lingane, Polarography, 2nd Ed. Vol. 1, Interscience Publishers, (New York), (1952) p. 178.

potential of an amalgam may be expressed as:

$$E = K - \frac{0.058}{n} (\log C_{H_2O} - \log C_{Hg})$$

It can be seen that by increasing the concentration of the metal in the amalgam the potential of the amalgam will be increased. The object of the test was also to determine the effect of increasing the copper content of the amalgam anode.

An amalgam , containing approximately 0.4 gm copper was prepared by electrolyzing 400 ml of 10 gm per liter copper sulfate. Fifty milliliters of 10 gm per liter copper chloride were placed in the cell and used as the electrolyte The results of this test was a dark copper colored deposit which was not adherent and peeled off and was dissolved. Diffraction studies of this substance showed it to be completely copper oxide (CuO). This test was not a complete success,,however it was a step in the right direction.

The next job was to determine whether the electrolyte or the increased concentration in the amalgam was the cause of the results and to prevent the oxidation of the deposit. A series of copper sulfate solutions of varying strengths were made up. An amalgam containing approximately 2% copper served as the anode. The solutions of compositions: 20 , 10 , 5 , 2.5 gm per liter were run at currents varying from 0.6 to 2.4 amps. In these tests the same amalgam was used throughout the series of four tests. These tests seemed

to indicate that the optimum results can be achieved from a system involving a concentrated amalgam, a concentrated electrolyte, and a low current density.

A test was made to verify the trend indicated above. An amalgam containing about 4 grams of copper was prepared by electrolyzing 400 ml of 10 gm per liter copper sulfate. This amalgam was made the anode in a refining cell containing 100 ml of 40 gm per liter copper sulfate. The current was set at 0.5 amps at a potential of 0.35 volts. Electrolysis was continued for 5hrs 21 min. This test was successful in producing metallic copper.

The final test was confined to determining the effect of elapsed time of electrolysis on current efficiency for the extraction of copper from the leach solution. The data from this and the other tests can be found in Section VI.

VI. DATA

Test No. 1

Object: To prepare an amalgam for furthur testing.

Electrolyte: 300 ml Kelly leach solution

Current: 1.75 amps

Voltage: 3.5 volts

Time: 30 min.

Current Efficiency: 65.8%

Test No. 2

Object: To remove copper from amalgam formed in test 1.

Electrolyte: 300 ml spent electrolyte approx 3N H_2SO_4

Remarks: The potential was varied from 0 v to a maximum of 11 v. Mercury was plated on copper cathode above 3.5 v. Aside from that,,no other action was noticed.

Test No 3

Object: To test a different electrolyte.

Electrolyte: 300 ml Kelly leach solution.

Remarks: The potential was varird from 0 to 11 volts. Mercury was plated out above 3.5 volts.

Test No. 4

Object: To prepare a pure amalgam

Electrolyte: 50 ml of 10 gm/l $CuSO_4$

Current: 1.24 amps.

Voltage: 2.5 volts

Time: 18 min.

Current Efficiency: 98.8%

Test No.5

Object: To remove the copper from amalgam no. 4

Electrolyte: 100 ml of 10 gm/l $CuSO_4$

Voltage: 0 to 11 volts

Remarks: The results of this test were the formation of $Hg_2(SO_4)$ and the plating of mercury on the copper cathode.

Test No. 6

Object: To determine the joint effect of a concentrated amalgam and a change in electrolyte.

Electrolyte: 50 ml of 10 gm/l $CuCl_2$

Current: 1.5 amps

Voltage: 5.0 volts

Remarks: The results of this test was a non-adherent coating of CuO.

Test No. 7

Object: To test another electrolyte.

Electrolyte: 50 ml of 3N HCl

Curremt; 0.75 amps

Voltage: 1.25 volts

Time: 5 min.

Results: A non adherent coating of CuO on the cathode.

Test No.8

Object: To test a more concentrated electrolyte.

Electrolyte: 100 ml of 20 gm/l $CuSO_4$

Current: 1.2 amps

Voltage: 2.5 volts

Time: 31 min.

Results; Diffraction methods indicated a mixture of Cu and

CuO .

Remarks: The amalgam contained about 1.97% copper.

Test No. 9

Object: To determine the effect of a change in current.

Electrolyte: 100 ml of 20 gm/l $CuSO_4$

Current: 2.4 amps

Voltage: 3.5 volts

Remarks: Copper Oxide formed on the cathode and fell off. The same amalgam was used in tests 8 and10

Test No. 10

Object: To determine the effect of a change in current.

Electrolyte: 100 ml of 20 gm/l $CuSO_4$

Current: 0.6 amps

Voltage: 0.5 volts

Time: 15 min.

Results: A non adherent coating of CuO

Remarks: The same amalgam was used in tests 8 and 9.

Test No. 11

Object: To test a different concentration of electrolyte.

Electrolyte: 100 ml of 2.5 gm/l $CuSO_4$

Current: 0.3 amp

Voltage: 1.25 volts

Remarks: This test was allowed to proceed until it was evident that the deposit was CuO.

Test No. 12

Object: To determine the effect of a change of current on the electrolysis of the solution electrolyzed in test No. 11.

Electrolyte: 100 ml of 2.5 gm/l $CuSO_4$

Current: 0.6 amp

Voltage: 1.90 volt

Remarks: Electrolysis was continued until it became evident that the deposit was CuO. The same amalgam as was in tests 8 through 12.

Test No. 13

Object: A continuation of tests 8 through 12 at a higher current density.

Electrolyte: 100 ml of 2.5 gm/l $CuSO_4$

Current: 1.2 amp

Voltage: 3.8 volts

Remarks: This test continued until it became evident that the deposit was CuO. The deposit would not stay on the cathode.

Test No. 14

Object: To observe the electrolysis involving an electrolyte of intermediate concentration.

Electrolyte: 100 ml of 5 gm/l $CuSO_4$

Current: 1.5 amps

Voltage: 0.8 volts

Remarks: The deposit formed was CuO. At this time it was decided that there was no more to be gained from this type of testing, so it was discontinued.

Note: (The procedure followed in tests 8 through 14 was as follows; The amalgam containing 1.97% copper was placed in the cell, the solution containing 20 gm/l $CuSO_4$ was placed in contact with the mercury in the cell. Electrolysis was then carried out at 1.2 amps. After a period of time, the cathode was stripped and replaced in the cell and electrolysis continued at 2.4 amps. The cathode was again stripped and the current changed to 0.6 amp. and then to 0.3 amp in succession. The solution was removed and replaced with 100 ml of 2.5 gm/l $CuSO_4$ and the procedure repeated. The same amalgam was used in all of these trials. Electrolysis was allowed to proceed only to the point where the nature of the deposit was ascertained.)

Test No. 15

Object: To investigate the trend indicated by the preceeding tests, that is, electrolysis in a system of a concentrated amalgam, a concentrated electrolyte, with a low current density.

Electrolyte: 100 ml of 40 gm/l $CuSO_4$

Current: 0.5 amps

Voltage: 0.35 volts

Time: 5 hr. 17 min.

Current Efficiency: 88.4%

Remarks: The deposit was very fine grained and rough. It oxidized partially upon exposure to the atmosphere.

Test No. 16

Object: To determine the variation of current efficiency of the electrowinning step with time.

Electrolyte: 200 ml of Kelly leach solution.

Current: 1.24 amps

Voltage: 3.0 volts

Time-min	Current Efficiency
5	75.0 %
10	75.0
15	83.8
20	97.6
25	88.6
45	88.8
55	97.3
75	97.3
85	99.4

Remarks: The current fluctuated greatly; it was difficult to maintain a constant current.

VII. DISCUSSION OF RESULTS

The testing indicates that the potential is the important consideration in refining the amalgam. This is evidenced by the failures of tests No's 2,3, and 5 and the success of test No. 15. In tests 2, 3, and5 , to obtain an appreciable current it was necessary to resort to higher voltages which resulted in the plating of the mercury.

The use of concentrated solutions effectively reduced the resistanceof the cell. This allowed the passage of a greater amount of current through the cell, for a given potential.

A lower current density could probably arrest the formation of CuO. Even on the cathode from test 15, which was successful, showed the formation of CuO on the corners which are areas of high current density. The current density could be lowered by the use of a larger cathode or lower currents. Howeverthere is a limit to how small a current can be used to be practical industrially. Thecopper must be plated out within a reasonable length of time. And a small current will deposit a smaller amount of metal in a given time than will a larger one.

During the testing, a scale formed upon the amalgam anode. It was not so apt to form at lower currents,but its

formation did not seem to follow any certain pattern. Some times it formed other times it did not. Qualitative analysis by X-Ray Spectroscopy showed that it was composed of mercury and copper. It is my belief that this product is a binary copper-mercury alloy

I would like to propose an explaination for the formation of this alloy. It is my belief that the copper in the amalgam migrates under the influence of the current to the surface where the amalgam becomes greately concentrated and solidified and separates. If this is the situation, this may be a problem to be solved before the process can be used industrially. One solution would be to keep the amalgam stirred. A magnetic stirrer could be used be used for this purpose.

The results of test No. 16 are difficult to explain. First, the current efficiencies are all higher than that of test No. 1 and secondly they indicate that the current efficiency increases with time. This is contrary to what would ordinarily be expected. The only explaination that can be given for this behavior is that the current was very erratic and hard to control. This is shown by the wide variation in current efficiency. They do, however , indicate an increasing current that is unexplainable.

VIII. CONCLUSIONS

The results of the investigation indicated several conclusions.

1. The electrodeposition of copper from the Kelly leach solutions is possible with good current efficiency.
2. Electrolysis of copper in a system containing a liquid amalgam anode is possible with fairly good current efficiency.
3. In a system involving a liquid amalgam anode, close control over the potential is necessary to prevent the deposition of mercury.
4. The application of amalgam metallurgy to the extraction of copper from its complex ores does show some promise and warrents further investigation.

IX. RECOMMENDATIONS FOR FURTHER STUDY

1. Further work should be carried out to establish the conditions necessary for high current efficiency.
2. More work should be done on improving the nature of the deposit.
3. Electrolysis should be attempted at variable conditions of temperature and pH. A study of the effect of the concentration of the metal in the amalgam would also be of value..
4. It would be advantageous to study the formation and the prevention of cell impurities such as the solid copper amalgam which formed during refining of the liquid amalgam.
5. An investigation into decomposition potentials of various amalgams would be of value in furthering the progress of amalgam metallurgy..

ACKNOWLEDGMENTS

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-APPENDIX-

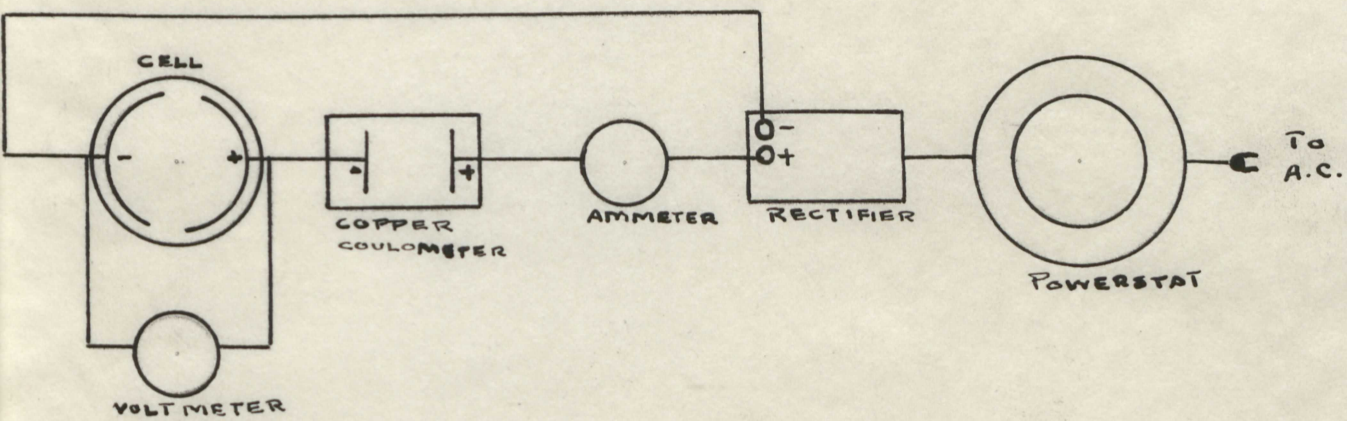

Figure No. 1 Electrical Circuit used in the Investigation

Figure No. 2 Leaching Equipment

Figure No. 3 Cell and Accessories